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(71) Applicant *(for all designated States except US)*: **SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.** [NL/NL]; Carel van Bylandlaan 30, NL-2596 HR The Hague (NL).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: **NULL, Volker, Klaus** [DE/DE]; Hohe-Schaar-Strasse 36, 21107 Hamburg (DE).

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(54) **Title:** SILICON RUBBER COMPRISING AN EXTENDER OIL AND PROCESS TO PREPARE SAID EXTENDER OIL

(57) **Abstract:** Silicon rubber composition comprising a hydrocarbon extender oil, wherein the oil is a Fischer-Tropsch derived oil. Process to prepare a silicon rubber extender oil having a CN number as measured according to IEC 590 of between 15 and 30%, a kinematic viscosity at 40 °C of between 5 an 18 mm²/sec.

# SILICON RUBBER COMPOSITION COMPRISING AN EXTENDER OIL AND PROCESS TO PREPARE SAID EXTENDER OIL

The invention is directed to a silicon rubber composition comprising a hydrocarbon extender oil. The invention is also directed to a process to make such an extender oil.

Process oils are used in silicon rubber compositions as a cheap extender oils to reduce formulation costs. Key requirements for process oils for this application are full silicon oil compatibility but also good UV stability and low volatility. Widely available extender oils used for this purpose are naphthenic oils and hydroprocessed paraffinic petroleum oils. Hydroprocessed paraffinic petroleum oils are preferred for this use.

A disadvantage of the use of hydroprocessed paraffinic petroleum oils is that although some oils show excellent UV stability they show less good silicon oil compatibility at higher oil contents.

The object of the present invention is to provide a silicon rubber composition wherein the content of extender oil can be increased while properties as UV stability and volatility are not worsened as compared to when a hydroprocessed paraffinic petroleum derived oil is used because of their low volatility and good UV stability.

This object is achieved by the following composition. Silicon rubber composition comprising a hydrocarbon extender oil, wherein the oil is a Fischer-Tropsch derived oil.

Applicants found that when the Fischer-Tropsch derived oil is used an improved UV stability, and lower weight loss is observed as compared to when the hydroprocessed paraffinic petroleum oils are used. Furthermore the Fischer-Tropsch derived oil is found to be very compatible with the silicon rubber, even at high oil contents. The latter is very advantageous for economic reasons because the composition may comprise more of the Fischer-Tropsch derived oils. It is known that naphthenics oils have good compatibility with silicon rubber. It was thus a surprising finding that a Fischer-Tropsch derived oil, which is expected to contain high amounts of paraffins, shows such good silicon rubber compatibility.

The Fischer-Tropsch derived oil preferably has a kinematic viscosity at 40 °C of between 5 and 18 $mm^2/sec$, and more preferably below 12 $mm^2/sec$. The pour point of the oil is preferably below -20 °C and more preferably below -30 °C. The sulphur content in the oil is preferably below 30 ppm and the nitrogen content is preferably below 100 ppm. Fischer-Tropsch derived oils will generally contain even lower levels of sulphur and nitrogen, preferably below 10 ppm ranges. Applicants further found that the Fischer-Tropsch derived oil preferably has a CN number as measured according to IEC 590 of between 15 and 30%.

Examples of processes, which can for example be used to prepare the above-described Fischer-Tropsch derived oils, are described in EP-A-776959, EP-A-668342, US-A-4943672, US-A-5059299 and WO-A-9920720. The process will generally comprise a Fischer-Tropsch synthesis, a hydroisomerisation step and an optional pour point

reducing step, wherein said hydroisomerisation step and optional pour point reducing step are performed as:

(a) hydrocracking/hydroisomerisating a Fischer-Tropsch product,

(b) separating the product of step (a) into at least one or more distillate fuel fractions and an extender oil fraction.

Optionally the pour point of the extender oil is further reduced in a step (c) by means of solvent or preferably catalytic dewaxing of the oil obtained in step (b) to obtain oil having the preferred low pour point.

Examples of Fischer-Tropsch synthesis processes steps to prepare said Fischer-Tropsch product and hydroisomerisation steps (a) are known from the so-called commercial Sasol process, the commercial Shell Middle Distillate Process or the non-commercial Exxon process.

A preferred process to prepare the process oil having the desired CN-values (according to IEC 590) is when the a Fischer-Tropsch derived feed or product used in step (a), which feed is characterized in that the weight ratio of compounds having at least 60 or more carbon atoms and compounds having at least 30 carbon atoms in the Fischer-Tropsch derived feed is at least 0.2 and wherein at least 30 wt% of compounds in the Fischer-Tropsch derived feed have at least 30 carbon atoms.

The relatively heavy Fischer-Tropsch derived feed as used in step (a) has at least 30 wt%, preferably at least 50 wt%, and more preferably at least 55 wt% of compounds having at least 30 carbon atoms. Furthermore the weight ratio of compounds having at least 60 or more carbon atoms and compounds having at least 30 carbon

atoms of the Fischer-Tropsch derived feed is at least 0.2, preferably at least 0.4 and more preferably at least 0.55. The Fischer-Tropsch derived feed is preferably derived from a Fischer-Tropsch product which comprises a $C_{20}+$ fraction having an ASF-alpha value (Anderson-Schulz-Flory chain growth factor) of at least 0.925, preferably at least 0.935, more preferably at least 0.945, even more preferably at least 0.955.

The initial boiling point of the Fischer-Tropsch derived feed may range up to 400 °C, but is preferably below 200 °C. Preferably at least compounds having 4 or less carbon atoms and compounds having a boiling point in that range are separated from a Fischer-Tropsch synthesis product before the Fischer-Tropsch synthesis product is used as a Fischer-Tropsch derived feed in step (a). The Fischer-Tropsch derived feed as described in detail above will for the greater part comprise of a Fischer-Tropsch synthesis product. In addition to this Fischer-Tropsch product also other fractions may be part of the Fischer-Tropsch derived feed. Possible other fractions may suitably be any high boiling fraction obtained in step (b).

Such a Fischer-Tropsch derived feed is suitably obtained by a Fischer-Tropsch process, which yields a relatively heavy Fischer-Tropsch product. Not all Fischer-Tropsch processes yield such a heavy product. An example of a suitable Fischer-Tropsch process is described in WO-A-9934917 and in AU-A-698392. These processes may yield a Fischer-Tropsch product as described above.

The hydrocracking/hydroisomerisation reaction of step (a) is preferably performed in the presence of hydrogen and a catalyst, which catalyst can be chosen

from those known to one skilled in the art as being suitable for this reaction. Catalysts for use in step (a) typically comprise an acidic functionality and a hydrogenation/dehydrogenation functionality. Preferred acidic functionalities are refractory metal oxide carriers. Suitable carrier materials include silica, alumina, silica-alumina, zirconia, titania and mixtures thereof. Preferred carrier materials for inclusion in the catalyst for use in the process of this invention are silica, alumina and silica-alumina. A particularly preferred catalyst comprises platinum supported on a silica-alumina carrier. If desired, the acidity of the catalyst carrier may be enhanced by applying a halogen moiety, in particular fluorine, or a phosphorous moiety to the carrier. Examples of suitable hydrocracking/hydro-isomerisation processes and suitable catalysts are described in WO-A-0014179, EP-A-532118 and the earlier referred to EP-A-776959.

Preferred hydrogenation/dehydrogenation functionalities are Group VIII metals, such a nickel, cobalt, iron, palladium and platinum. Preferred are the noble metal Group VIII members, palladium and more preferred platinum. The catalyst may comprise the more preferred noble metal hydrogenation/dehydrogenation active component in an amount of from 0.005 to 5 parts by weight, preferably from 0.02 to 2 parts by weight, per 100 parts by weight of carrier material. A particularly preferred catalyst for use in the hydroconversion stage comprises platinum in an amount in the range of from 0.05 to 2 parts by weight, more preferably from 0.1 to 1 parts by weight, per 100 parts by weight of carrier material. The catalyst may also comprise a binder to enhance the strength of the catalyst. The binder can be non-acidic.

Examples are clays and other binders known to one skilled in the art.

In step (a) the feed is contacted with hydrogen in the presence of the catalyst at elevated temperature and pressure. The temperatures typically will be in the range of from 175 to 380 °C, preferably higher than 250 °C and more preferably from 300 to 370 °C. The pressure will typically be in the range of from 10 to 250 bar and preferably between 20 and 80 bar. Hydrogen may be supplied at a gas hourly space velocity of from 100 to 10000 Nl/l/hr, preferably from 500 to 5000 Nl/l/hr. The hydrocarbon feed may be provided at a weight hourly space velocity of from 0.1 to 5 kg/l/hr, preferably higher than 0.5 kg/l/hr and more preferably lower than 2 kg/l/hr. The ratio of hydrogen to hydrocarbon feed may range from 100 to 5000 Nl/kg and is preferably from 250 to 2500 Nl/kg.

The conversion in step (a) as defined as the weight percentage of the feed boiling above 370 °C which reacts per pass to a fraction boiling below 370 °C, is at least 20 wt%, preferably at least 25 wt%, but preferably not more than 80 wt%, more preferably not more than 65 wt%. The feed as used above in the definition is the total hydrocarbon feed fed to step (a), thus also any optional recycle of a high boiling fraction which may be obtained in step (b).

In step (b) the product of step (a) is preferably separated into one or more distillate fuels fractions and an extender oil (precursor) fraction having the desired viscosity properties. In a preferred embodiment the pour point of the extender oil is further reduced by means of a catalytic dewaxing step (c). In such an embodiment it may be a further advantage to dewax a wider boiling fraction of the product of step (a). From the resulting

dewaxed product the extender oil and oils having a higher viscosity can then be advantageously isolated by means of distillation. The final boiling point of the feed to the dewaxing step (c) may be up to the final boiling point of the product of step (a).

The silicon rubber component may be a state of the art silicon rubber as described in Rubber Technology Handbook, Werner Hofmann, Oxford University Press, New York, 1980, paragraph 3.4.1. Silicon rubbers have a main polymer chain, which mainly consist of silicon and oxygen atoms. On the silicon atoms in the chain hydrocarbon groups like for example methyl, ethyl or phenyl may be present. Small amounts of termonomer with vinyl groups may also be present in the rubber. Next to the silicon rubber and the extender oil vulcanizing agents, fillers, stabilizers and softeners may also be present in the silicon rubber composition.

The silicon rubber content will be between 90 and 60 wt%. The extender oil content will preferably be between 10 and 40 wt% and more preferably between 20 and 40 wt% and most preferably above 30 wt%.

The invention will be illustrated by making use of the following non-limiting examples.

Table 1:

| Oils tested | | | Fischer-Tropsch derived oil | Total Hydroseal G 400 H |
|---|---|---|---|---|
| | Method | Unit | | |
| DENSITY at 15 °C | DIN 51757 | $kg/m^3$ | 803,4 | 812,4 |
| REFRACTIVE INDEX at 20 °C | DIN 51423-2 | | 1,4468 | 1,4472 |
| POUR POINT | DIN ISO 3016 | °C | <-63 | -45 |
| KIN.VISCOSITy 40 °C | DIN 51562 | mm2/s | 6,8 | 6,0 |
| CN number | IEC 590 | % | 24.9 | Not measured |

Example 1

30 PHR of a Fischer-Tropsch derived oil having the properties as listed in Table 1 was thoroughly mixed for 10 minutes by means of a turbo mixer (approx. 1500 rpm) with 70 PHR of a silicon rubber (Wacker Silicon rubber NG 200-120000) and 5 PHR of a coupling agent and catalyst (Wacker coupling agent ES 24)

Oil compatibility

20 g of the mixture as obtained above was placed on an OHP slide, spread with a spatula to give a layer with 1-3 mm thickness. The surface was evaluated after 3 days of connecting up at room temperature (20 °C). The surface was observed to be smooth and dry without any observation of oil drops.

Weight loss

Approximately 25 g of the freshly prepared oil-silicon mixture as obtained after turbo mixing was weighted in an Aluminium pan to the nearest 0.1 mg (Aluminium pan with 28 ml volume, lower diameter 51 mm, upper diameter 64 mm). The weight loss is determined from two samples after 21 days, first 7 days storage at room temperature (20 °C) followed by 14 days at 70 °C. The results are summarized in Table 2.

UV stability of the oil

The Fischer-Tropsch derived oil was also evaluated in a UV light box and monitored daily. It was found that the oil sample remained clear (by visional observation) for at least 264 hours.

Example 2

Example 1 was repeated except that 32.5 PHR of Fischer-Tropsch derived oil was used. The weight percentage of coupling agent was the same as in Example 1.

Oil compatibility

The surface was observed to be smooth and dry without any observation of oil drops.

Example 3

Example 1 was repeated except that 35 PHR of Fischer-Tropsch derived oil was used. The weight percentage of coupling agent was the same as in Example 1. The results are presented in Table 2. The surface was observed to be smooth and dry without any observation of oil drops.

Comparative experiment A

Example 1 was repeated except that a Total Hydroseal G 400 H oil was used as extender oil. The properties of this oil are also listed in Table 1. The

surface was observed to be smooth and dry without any observation of oil drops.

Weight loss

The weight loss results as determined after the full 21 days, are summarized in Table 2.

UV stability of the oil

The Hydroseal G 400 H oil was also evaluated in a UV light box and monitored daily. It was found that the oil sample remained clear (by visional observation) for 168 hours. After 192 hours a haze was observed.

Comparative Experiment B

Example 2 was repeated except that Total Hydroseal G 400 H oil was used as extender oil. The surface was observed to separate oil drops resulting from oil leaking from the oil extended silicon rubber.

The composition was not stable and the oil was not compatible with the silicon rubber at the oil content as tested.

Comparative Experiment C

Example 3 was repeated except that a Total Hydroseal G 400 H oil was used as extender oil. The surface was observed to separate oil drops resulting from oil leaking from the oil extended silicon rubber.

The composition was not stable and the oil was not compatible with the silicon rubber at the oil content as tested.

Table 2

| Weight loss results | | Fischer-Tropsch derived oil | Total Hydroseal G 400 H |
|---|---|---|---|
| | | | |
| 30% Oil in Silicon Rubber | wt% | 8,7 (Example 1) | 15 (Experiment A) |
| 32,5% Oil in Silicon Rubber | wt% | 7,4 (Example 2) | * |
| 35% Oil in Silicon Rubber | wt% | 9,1 (Example 3) | * |

* the weight loss was not determined because no stable polymer was obtained at these high oil contents.

C L A I M S

1. Silicon rubber composition comprising a hydrocarbon extender oil, wherein the oil is a Fischer-Tropsch derived oil.

2. Composition according to claim 1, wherein the kinematic viscosity at 40 °C of the oil is between 5 and 18 $mm^2/sec$.

3. Composition according to claim 2, wherein the kinematic viscosity at 40 °C of the oil is between 5 and 12 $mm^2/sec$.

4. Composition according to any one of claims 1-3, wherein the pour point of the oil is below -20 °C.

5. Composition according to any one of claims 1-4, wherein the CN number of the oil as measured according to IEC 590 is between 15 and 30%.

6. Composition according to any one of claims 1-5, wherein the oil content in the composition is between 20 and 40 wt%.

7. Composition according to any one of claims 1-6, wherein the oil is obtained by

(a) hydrocracking/hydroisomerisating a Fischer-Tropsch product,

(b) separating the product of step (a) into at least one or more fuel fractions and an extender oil fraction.

8. Composition according to claim 7, wherein the extender oil has also been subjected to a catalytic dewaxing treatment.

9. Process to prepare a silicon rubber extender oil having a CN number as measured according to IEC 590 of

between 15 and 30%, a kinematic viscosity at 40 °C of between 5 an 18 $mm^2$/sec by
(a) hydrocracking/hydroisomerisating a Fischer-Tropsch product,
(b) separating the product of step (a) into at least one or more fuel fractions and an extender oil precursor fraction and (c) reducing the pour point of the extender oil precursor fraction to obtain, optionally after separation of heavier and lighter by-products, the extender oil having a pour point of below - 20 °C.

# INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/07861

**A. CLASSIFICATION OF SUBJECT MATTER**
IPC 7 C10G67/04 C08L83/04

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C10G C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| X | WO 97 21788 A (EXXON RESEARCH ENGINEERING CO) 19 June 1997 (1997-06-19) page 11, paragraph 1; claims 1,2; table 3 | 9 |
| X | EP 0 776 959 A (SHELL INT RESEARCH) 4 June 1997 (1997-06-04) cited in the application column 3, line 30 - line 42; claims 1,10; example 3 | 9 |

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 22 September 2003 | 01/10/2003 |

| Name and mailing address of the ISA | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL – 2280 HV Rijswijk<br>Tel. (+31–70) 340–2040, Tx. 31 651 epo nl,<br>Fax: (+31–70) 340–3016 | Deurinck, P |

## INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/07861

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| X | EP 0 321 305 A (EXXON RESEARCH ENGINEERING CO) 21 June 1989 (1989-06-21)<br>claims 1,9; figures 1,2<br>--- | 9 |
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**FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210**

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-8

   a silicon rubber composition comprising an extender oil, wherein the oil is a Fischer-Tropsch derived oil

2. Claim : 9

   a process to prepare a silicon rubber extender oil

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 03/07861

**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. [ ] Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. [ ] Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. [ ] Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. [ ] As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. [X] As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. [ ] As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. [ ] No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

[ ] The additional search fees were accompanied by the applicant's protest.

[ ] No protest accompanied the payment of additional search fees.

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 03/07861

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